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Published in:
Chemical Engineering Science

DOI:
[10.1016/0009-2509\(91\)85036-W](https://doi.org/10.1016/0009-2509(91)85036-W)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1991

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Citation for published version (APA):

Littel, R. J., Versteeg, G. F., & Swaaij, W. P. M. V. (1991). Physical absorption into non-aqueous solutions in a stirred cell reactor. *Chemical Engineering Science*, 46(12), 3308-3313. [https://doi.org/10.1016/0009-2509\(91\)85036-W](https://doi.org/10.1016/0009-2509(91)85036-W)

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Physical absorption into non-aqueous solutions in a stirred cell reactor

(First received 19 November 1990; accepted in revised form 23 April 1991)

1. INTRODUCTION

Many authors have reported kinetic experiments in both aqueous and non-aqueous solutions which were carried out in a stirred cell reactor with a smooth horizontal gas-liquid interface (e.g. Sharma, 1965; Blauwhoff *et al.*, 1984; Sada *et al.*, 1985, 1986; Haimour *et al.*, 1987; Versteeg and van Swaaij, 1988a; Littel *et al.*, 1990).

Deduction of kinetic rate constants from gas absorption experiments can be very complex as a lot of interacting phenomena are involved. Therefore, extensive characterisation of a model reactor by means of physical absorption before carrying out reaction enhanced absorption experiments must be considered as indispensable. Physical absorption experiments in aqueous solutions have been presented by Versteeg *et al.* (1987) for the stirred cell reactor applied in the kinetic experiments reported by Blauwhoff *et al.* (1984), Versteeg and van Swaaij (1988a, b), Bosch *et al.* (1990) and Littel *et al.* (1990). Versteeg *et al.* (1987) reported a Sh, Sc, Re relationship and observed that the stirrer position relative to the gas-liquid interface did not affect the mass transfer coefficients. The relationship reported by Versteeg *et al.* (1987) between the liquid phase mass transfer rate and the stirrer speed was similar to the observations presented by Davies *et al.* (1964), Kozinski and King (1966), Linek *et al.* (1970), and Al-Ghawas (1988). So far, for stirred cell reactors with a smooth horizontal gas-liquid interface physical absorption experiments in only aqueous solutions seem to have been reported.

In the present work physical absorption of CO_2 and N_2O into non-aqueous solutions has been studied in the same type of stirred cell reactor as studied by Versteeg *et al.* (1987). The stirrer position relative to the gas-liquid interface was systematically varied. Absorption experiments of CO_2 in methanol, ethanol, 1 propanol, 1-butanol and 1-octanol and absorption experiments of N_2O into water and DEA/ethanol solutions (0.7 M, 1.4 M, 2.4 M, 3.3 M) are reported.

2. EXPERIMENTAL

2.1. Experimental setup

All absorption experiments were carried out in a thermostatted all-glass stirred cell reactor with a smooth and horizontal gas-liquid interface. The total volume of the reactor was 1328 ml and the interfacial surface area was $72 \times 10^{-4} m^2$. Four 8 mm baffles in the reactor helped to ensure the smoothness of the gas-liquid interface. The reactor was operated batchwise with respect to both gas and liquid phase. The reactor pressure was measured by means of a pressure transducer. For all absorption experiments the initial reactor pressure was about 0.9×10^5 Pa. Gas phase resistance could be neglected as all experiments were carried out with pure gas.

The reactor was stirred by means of a glass stirrer which consisted of six stirrer blades mounted on one shaft. The size of each stirrer blade was about $68 \times 10 \times 2 mm^3$; spacing between two stirrer blades was about 12 mm. Two glass embedded magnetic bars were also attached to the shaft. Magnetic coupling with a variable speed motor allowed for precise regulation of the stirring speed. Six positions of the stirrer relative to the gas-liquid interface were studied (see also Fig. 1):

- position 1: stirrer blade 1 just submerged in liquid
- position 2: stirrer blade 2 just above gas-liquid interface
- position 3: stirrer blade 2 just submerged in liquid
- position 4: stirrer blade 3 just above gas-liquid interface
- position 5: stirrer blade 3 just submerged in liquid
- position 6: stirrer blade 4 just above gas-liquid interface.

All absorption experiments were carried out in the same stirred cell reactor. Detailed information concerning the experimental procedure can be found elsewhere (Blauwhoff *et al.*, 1984; Versteeg and van Swaaij, 1988a).

2.2. Theory

Based on mass balances for both the gas and the liquid phase the following expression can be derived for the pressure decrease owing to physical absorption as a function of time:

$$\ln \left(\frac{P(t) - P^\infty}{P^0 - P^\infty} \right) = - \frac{(mV_L + V_g)}{V_L V_g} k_L A t. \quad (1)$$

From this relationship between pressure decrease and time, the liquid phase mass transfer coefficient k_L can be easily calculated. The absorption experiments for determining the k_L -value were allowed to reach equilibrium in order to obtain the dimensionless solubility:

$$m = \frac{(P^0 - P^\infty) V_g}{(P^\infty - P_{vap}) V_L}. \quad (2)$$

It is common practice to try to describe the dependence of the experimentally observed mass transfer coefficients on hydrodynamics and molecular diffusivity by means of a power law relationship of dimensionless numbers. For liquid phase controlled physical absorption into aqueous solutions

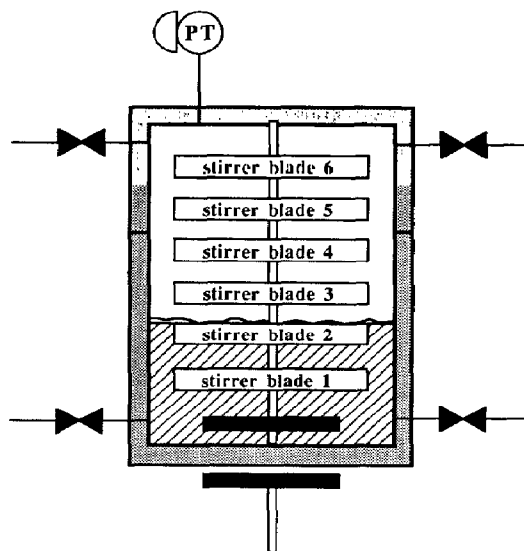


Fig. 1. Stirred cell reactor (stirrer position 3 indicated).

in a stirred cell reactor, Versteeg *et al.* (1987) reported a Sh , Sc , Re relationship:

$$Sh = c_1 Re^{0.72} Sc^{c_2} \quad (3)$$

with

$$Sh = \frac{d_s k_L}{D}, \quad Sc = \frac{\eta}{\rho D}, \quad Re = \frac{d_s^2 N \rho}{\eta} \quad (4)$$

The values of c_1 and c_2 were reported to range from 0.181 and 0.33, for small Sc numbers, to 0.064 and 0.5, for large Sc numbers. The 0.72 power dependence of the Sh number on the Re number was a mean value based on observations ranging from 0.66 to 0.76.

Machon and Linek (1974) presented a power law relationship of dimensionless numbers to correlate their experimental data for the physical absorption of oxygen and helium into aqueous solutions of inorganic electrolytes. In their relationship also surface and electric forces were taken into account. The variation in their gas-solvent combinations, however, seems to be rather limited with respect to the number of effects which have been taken into account in this relationship.

Viscosity, density, surface tension, solubility and diffusivity data for the non-aqueous solutions applied in the present work are presented in Table 1. These data were obtained either by direct measurement or from literature (Handbook, 1982; Takahashi and Kobayashi, 1982; Versteeg and van Swaaij, 1988a).

3. RESULTS

3.1. H_2O

In order to characterise the present stirred cell reactor with respect to the Sh , Sc , Re relationship reported by Versteeg *et al.* (1987) for a similar stirred cell reactor, absorption experiments of N_2O into water were carried out prior to the absorption experiments into non-aqueous solutions. The measured k_L values, which were reproducible within about 10%, are presented in Fig. 2. No influence of the position of the stirrer blades relative to the gas-liquid interface was observed.

The observed power dependence of k_L on the stirring rate was about 0.75 which is in close agreement with the value of 0.72 reported by Versteeg *et al.* (1987). Moreover the measured k_L values also coincide with their Sh , Sc , Re relationship. From the absorption experiments of N_2O into water it can be concluded that the phenomena observed by Versteeg *et al.* (1987) for aqueous solutions also hold for the present stirred cell reactor.

3.2. Primary alcohols

Absorption of CO_2 into methanol, ethanol, 1-propanol, 1-butanol and 1-octanol was studied at 298 K. The stirrer position relative to the gas-liquid interface was varied systematically.

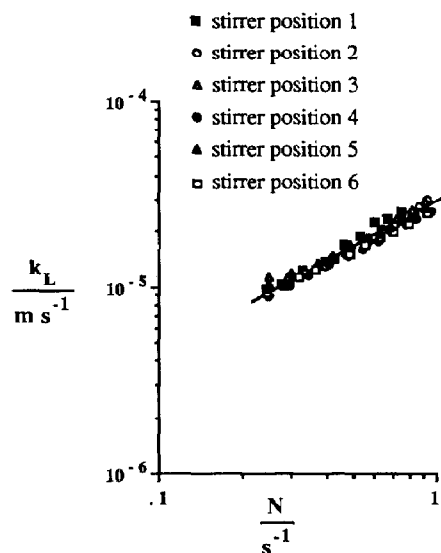


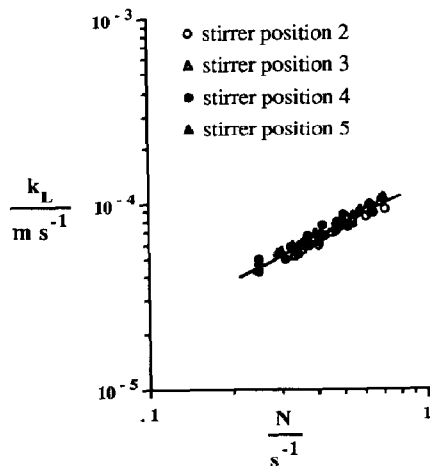
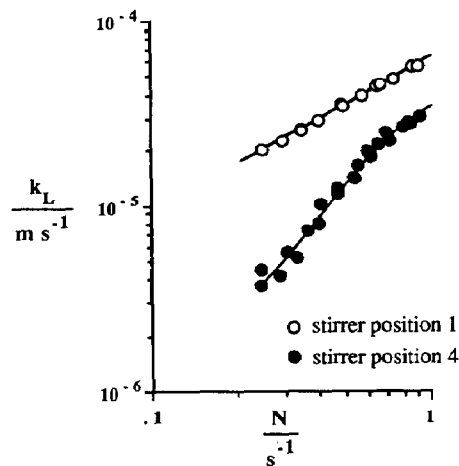
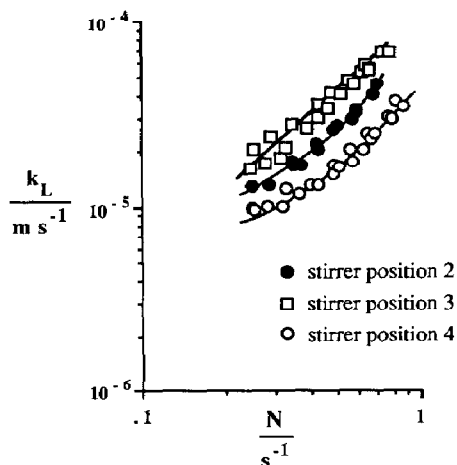
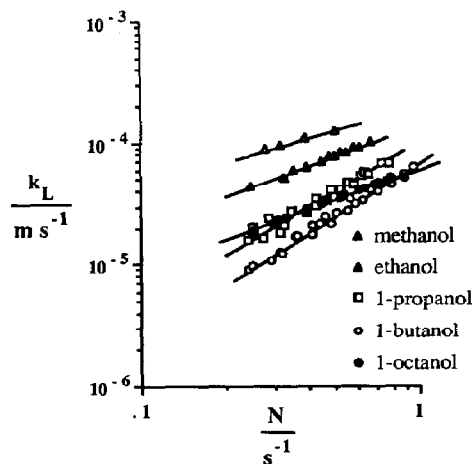
Fig. 2. Experimental absorption data for N_2O/H_2O .

The experimental results for ethanol are reported in Fig. 3. From this figure it can be concluded that no significant influence of the stirrer position was observed and that the power dependence of the k_L value on the stirring rate was very similar to the dependence reported for aqueous solutions. In Fig. 4 experimental results for 1-propanol are presented for three stirrer positions. Obviously, for 1-propanol the position of the stirrer relative to the gas-liquid interface does have a significant influence on the liquid phase mass transfer coefficient. Moreover, also the power dependence of the k_L value on the stirring rate is much larger than for aqueous systems. For stirrer position 3 this dependence amounts to about 1.35 in comparison to 0.72 reported for aqueous solutions. The influence of the stirrer position relative to the gas-liquid interface on the liquid phase mass transfer coefficient is even more striking for the absorption experiments in 1-octanol as can be seen in Fig. 5.

In Fig. 6 the observed k_L values for the various primary alcohols are compared to each other at one stirrer position. Going from methanol to 1-octanol, the observed k_L value at a constant stirring rate should decrease as a result of the decreasing diffusivity and increasing viscosity. However, at the same stirring speed the observed k_L values for the 1-octanol system are actually even higher than those observed for 1-butanol.

Table 1. Physical constants for the systems applied

System	T (K)	ρ ($kg\ m^{-3}$)	η ($10^3\ Pa\ s$)	σ ($10^3\ N\ m^{-1}$)	m (dimensionless)	D ($10^9\ m^2\ s^{-1}$)
N_2O/H_2O	298	997	0.89	72.2	0.59	1.95
CO_2 /methanol	298	787	0.55	22.2	3.92	4.54
CO_2 /ethanol	298	785	1.08	22.7	2.78	3.86
CO_2 /1-propanol	298	800	1.97	23.4	2.15	3.06
CO_2 /1-butanol	298	806	2.60	24.2	1.91	2.50
CO_2 /1-octanol	298	823	7.35	27.1	1.42	1.53
N_2O /0.7 M DEA/ethanol	293	816	1.62	—	3.03	1.57
N_2O /1.4 M DEA/ethanol	293	829	2.21	—	2.82	1.44
N_2O /2.4 M DEA/ethanol	293	866	3.32	—	2.57	1.07
N_2O /3.3 M DEA/ethanol	293	896	5.47	—	2.24	0.87

Fig. 3. Experimental absorption data for CO₂/ethanol.Fig. 5. Experimental absorption data for CO₂/1-octanol.Fig. 4. Experimental absorption data for CO₂/1-propanol.Fig. 6. Experimental data for the absorption of CO₂ into primary alcohols (stirrer position 3).

3.3. DEA/ethanol systems

The absorption of N₂O into solutions of DEA (0.7 M, 1.4 M, 2.4 M, 3.3 M) in ethanol has been studied at 293 K. The stirrer position relative to the gas-liquid interface was varied systematically.

In Figs 7 and 8 the experimental results for different stirrer positions are presented for 1.4 M DEA and 3.3 M DEA, respectively. For both solutions a significant influence of the stirrer position relative to the gas-liquid interface was observed. The power dependence of the k_L values on the stirring rate ranged from 0.74 for the 1.4 M DEA solution for stirrer positions 1 and 3 up to 1.12 for the 3.3 M DEA solution for stirrer position 2.

Experimental results for the four solutions studied are compared to each other for two different stirrer positions in Figs 9 and 10, respectively. From these figures it can be concluded that the power dependence of the k_L value on the stirring rate seems to increase with increasing DEA concentration. In Fig. 9 the observed k_L value at a constant stirring speed is shown to decrease with increasing DEA concentra-

tion as can be anticipated from the diffusivity and viscosity data. In Fig. 10, however, at low stirring rates the observed k_L value for the 2.4 M DEA solution is significantly lower than the k_L value observed for the 3.3 M DEA solution.

3.4. Discussion

The present physical absorption experiments into non-aqueous solutions in a stirred cell reactor cannot be described by the Sh , Sc , Re relationship which was presented by Versteeg *et al.* (1987) for physical absorption into aqueous solutions in a similar stirred cell reactor. This is clearly illustrated in Fig. 11 in which the Sh , Sc , Re relationship reported by Versteeg *et al.* (1987) is plotted together with the presently observed liquid phase mass transfer coefficients at a stirring speed of $N = 0.5 \text{ s}^{-1}$ and stirrer position 3. From this figure it is also concluded that, although physical absorption into methanol and ethanol seemingly behaved like physical absorption into aqueous solutions, the observed liquid phase mass transfer coefficients at a constant stirring speed are much higher than those predicted on the

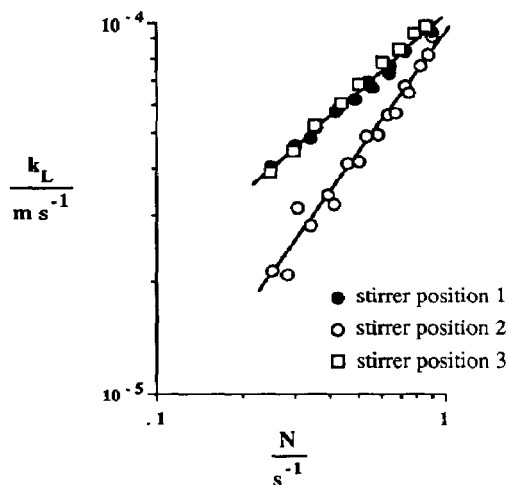


Fig. 7. Experimental absorption data for $N_2O/1.4$ M DEA/ethanol.

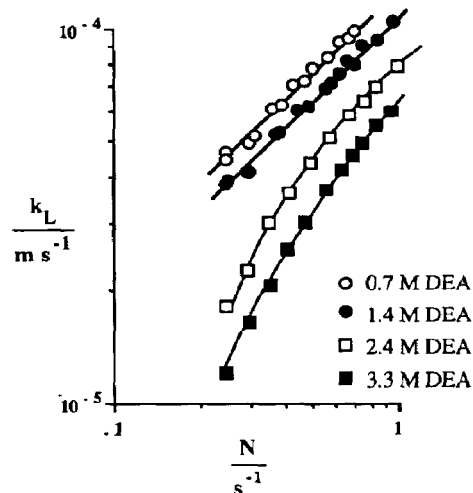


Fig. 9. Experimental data for the absorption of N_2O into DEA/ethanol solutions (stirrer position 5).

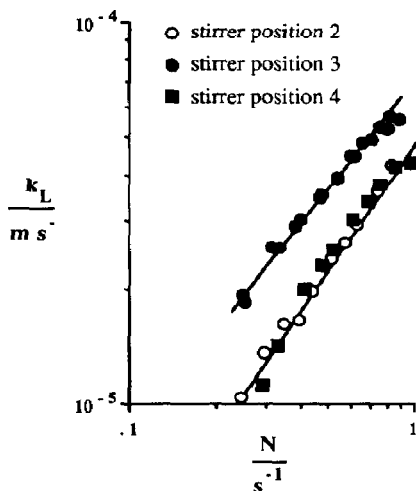


Fig. 8. Experimental absorption data for $N_2O/3.3$ M DEA/ethanol.

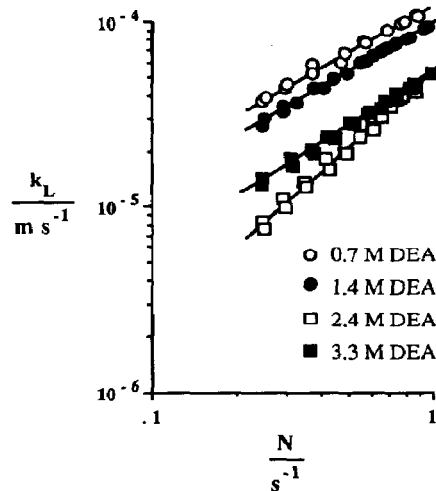


Fig. 10. Experimental data for the absorption of N_2O into DEA/ethanol solutions (stirrer position 6).

basis of changes in density, viscosity and diffusivity relative to aqueous solutions. The same phenomenon was observed by Hozawa *et al.* (1984) for the absorption of CO_2 in methanol and toluene in a two-dimensional source flow cell. They attributed the observed phenomena to the occurrence of Marangoni type turbulence.

It should be pointed out that the diffusion coefficient presented in Table 1 for CO_2 in 1-octanol was obtained from physical absorption experiments in a laminar film reactor. As this diffusion coefficient is well in line with diffusion coefficients for CO_2 in other primary alcohols and in water, it may be concluded that the phenomena which enhance physical absorption into primary alcohols in a stirred cell reactor do not occur in a laminar film reactor.

From the present experimental data for methanol and ethanol in comparison to experimental data for water it may be concluded that a Sh, Sc, Re relationship does not describe all phenomena which affect the liquid phase mass transfer

coefficient. An important parameter which is not included in such a relationship seems to be the surface tension. The surface tension may be regarded as a measure of the rigidity of the gas-liquid interface. The effectiveness of eddies caused by the stirrer with respect to surface renewal will probably increase with decreasing surface rigidity. In fact, the Levich treatment of mass transfer at free gas-liquid interfaces predicts that the liquid phase mass transfer coefficient depends linearly on the reciprocal square root of the surface tension (see Davies and Lozano, 1979). However, the presently observed mass transfer rates into non-aqueous solutions in a stirred cell reactor cannot be explained entirely from differences in surface tension of the different solutions. This can easily be seen from the comparison of the absorption experiments for 1-butanol and 1-octanol if it is considered that the surface tension of 1-octanol is somewhat higher than that of 1-butanol (see Table 1 and Figs 6 and 11).

Therefore, it must be concluded that apart from the

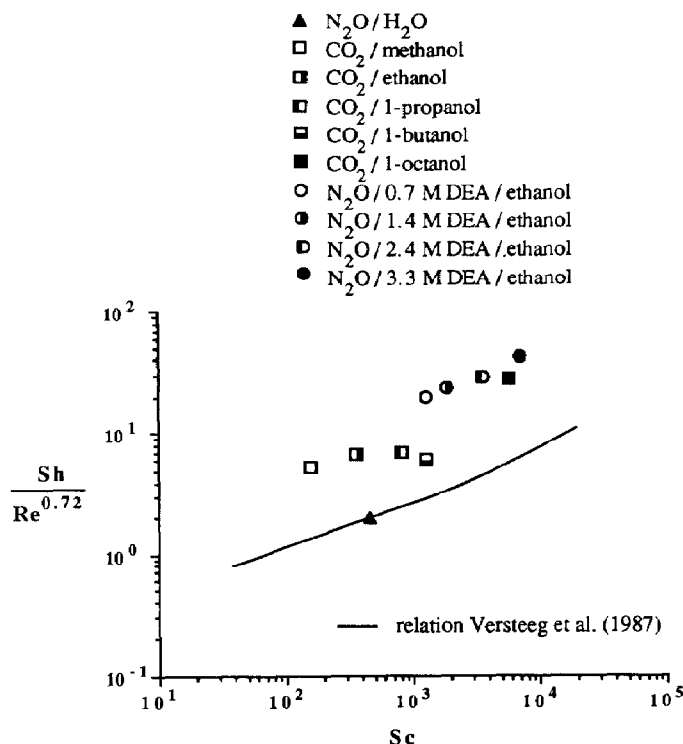


Fig. 11. Comparison of present experimental data with Sh , Sc , Re relationship reported by Versteeg *et al.* (1987) ($N = 0.5 \text{ s}^{-1}$, stirrer position 3).

turbulence caused by the stirrer, additional phenomena seem to have a significant contribution to the observed mass transfer rate. The nature of these additional interfacial turbulence phenomena is not clear and the present data for gas absorption into non-aqueous solutions in a stirred cell reactor cannot be understood in terms of common mass transfer theories. Explanations from surface tension effects or from Marangoni and Rayleigh effects should be regarded speculative at this moment, as there is no unambiguous evidence for the occurrence of these phenomena. Nevertheless, the present work shows the extreme importance for characterisation of model reactors by means of physical absorption experiments.

The present work on physical absorption into non-aqueous solutions in a stirred cell reactor may contain implications for kinetic experiments with non-aqueous or partially non-aqueous solvents in stirred cell reactors. These experiments should be interpreted carefully as it is not clear to what extent chemically enhanced absorption is affected by interfacial turbulence effects. Some authors have observed interfacial turbulence under reaction conditions (Linek, 1972; Linek and Hrma, 1976; Sada *et al.*, 1977). Interfacial turbulence seems to be strongly geometry-dependent as can be seen from the influence of the stirrer position on the mass transfer rate in the present work. It can be anticipated that also aqueous amine solutions may exhibit the same behaviour above a certain amine concentration. This is clearly illustrated by physical absorption experiments of N_2O in a concentrated methyldiethanolamine/ H_2O solution which are presented in Fig. 12. A power dependence of the k_L values on the stirring rate of about 1.0 was observed for this system.

4. CONCLUSIONS

The absorption of CO_2 and N_2O into non-aqueous solutions has been studied in a stirred cell reactor. Non-aqueous

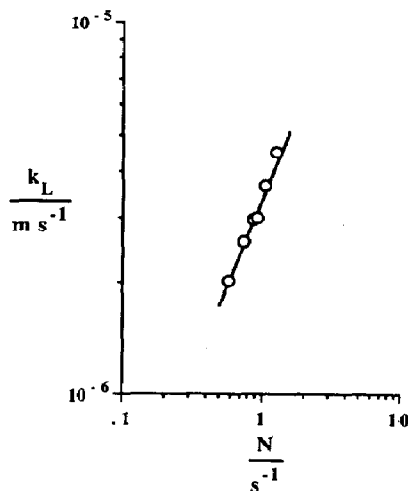


Fig. 12. Experimental absorption data for $N_2O/8.45 \text{ M MDEA}/H_2O$ (stirrer position 4).

solutions applied were primary alcohols and solutions of DEA in ethanol. It was shown that for most of these solutions the stirrer position relative to the gas-liquid interface does have a significant effect on the liquid phase mass transfer coefficient, whereas for aqueous systems no influence of the stirrer position on the mass transfer rate is observed [Versteeg *et al.* (1987); confirmed in the present work]. The experimentally observed k_L values were much higher than predicted by the Sh , Sc , Re relationship presented by Versteeg *et al.* (1987) for aqueous systems.

The present work shows that extensive characterisation of a model reactor by means of physical absorption before carrying out reaction enhanced absorption experiments is very important.

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Acknowledgements—These investigations were supported by the Koninklijke/Shell Laboratorium Amsterdam, The Netherlands. We also acknowledge H. Kreulen for providing absorption data of N_2O in a concentrated MDEA/ H_2O solution.

NOTATION

A	interfacial area, m^2
D	diffusivity, $m^2 s^{-1}$
d_s	stirrer diameter, m
k_L	liquid phase mass transfer coefficient, $m s^{-1}$
m	dimensionless solubility, $mol mol^{-1}$
N	stirring speed, revolutions s^{-1}
P^0	initial pressure, Pa
P_{vap}	vapor-liquid equilibrium pressure, Pa
P^∞	equilibrium pressure, Pa
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	time, s
V_g	gas volume, m^3
V_L	liquid volume, m^3

Greek letters

η	viscosity, $Pa s$
ρ	density, $kg m^{-3}$
σ	surface tension, $N m^{-1}$

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